



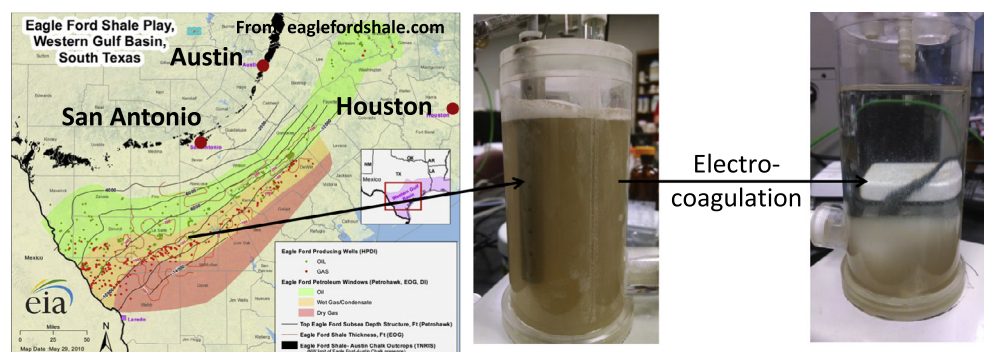
# Mechanisms of boron removal from hydraulic fracturing wastewater by aluminum electrocoagulation



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## GRAPHICAL ABSTRACT



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## ABSTRACT

**Hypotheses:** Boron uptake from highly saline hydraulic fracturing wastewater by freshly precipitated amorphous  $\text{Al}(\text{OH})_3$  precipitates is due to ligand exchange and complexation with surface hydroxyl groups. Consequently, aluminum electrocoagulation can be a feasible approach to remove boron from flowback/produced water.

**Experiments:** Actual hydraulic fracturing wastewater containing  $\sim 120$  mg/L boron from the Eagle Ford shale play was employed. Electrocoagulation was performed over a range of aluminum dosages (0–1350 mg/L), pH 6.4 and 8, and high current densities (20–80  $\text{mA}/\text{cm}^2$ ) using a cylindrical aluminum anode encompassed by a porous cylindrical 316-stainless steel cathode. Direct measurements of boron uptake along with its chemical state and coordination were made using Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR) and X-Ray Photoelectron Spectroscopy.

**Findings:** Boron removal increased monotonically with aluminum dosage and was higher at pH 8, but remained relatively constant at  $\geq 20$   $\text{mA}/\text{cm}^2$ . Chloride ions induced anodic pitting and super-Faradaic (131% efficiency) aluminum dissolution and their electrooxidation produced free chlorine. ATR-FTIR suggested outer-sphere and inner-sphere complexation of trigonal  $\text{B}(\text{OH})_3$  with  $\text{Al}(\text{OH})_3$ , which was confirmed by the B–O bond shifting toward lower binding energies in XPS. Severe Al–O interferences precluded evidence for tetrahedral  $\text{B}(\text{OH})_4^-$  complexation. No evidence for co-precipitation was obtained.

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## 1. Introduction

The explosive growth in the exploration and production of oil and gas from unconventional sources is associated with significant

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water management issues [1]. One increasingly popular well stimulation method is hydraulic fracturing (or fracking) wherein large quantities of water mixed with a proppant and other chemicals is injected into the subsurface at high pressure to unlock hydrocarbons [2]. This environmentally controversial technique produces copious amounts of briny wastewater consisting of a mixture of the injected fluid, local groundwater, and hydrocarbons. Concerns regarding high water consumption, environmental impacts of local wastewater discharge, onsite (waste)water trucking, and the desire to reuse water have resulted in growing regulatory and technological interest in treating flowback and produced water [3,4].

One of the myriad chemicals used in fracturing fluids is boron, which is used as a cross-linking agent to impart the necessary rheological properties to successfully deliver the proppant to fracture the rock and also to recover the injected fluid after fracking. Although boron is essential for plant growth and is a possible human trace nutrient, chronic exposure even at low doses causes testicular atrophy, decreased survival, and developmental and reproductive toxicity in animals [5]. Some crops such as blackberry are sensitive to even low (<0.5 mg/L) levels of boron while many other fruits and vegetables experience toxicity at concentrations >0.5 mg/L [6,7]. Boron containing viscosity modifiers also need to be removed from the flowback/produced water to make the reused water compatible with “gel-frac” formulations to fracture subsequent wells [1]. Therefore, boron is an element of concern which needs to be removed from hydraulic fracturing wastewater before it can be beneficially reused for crop irrigation, reused to frack additional wells, or discharged into receiving surface waters [6,8,9].

Ion exchange, electrocoagulation, adsorption onto clays and double-layered hydroxides have been shown to be effective for boron removal from low-salinity wastewater [6,10–13]. Low concentrations of boron can also be effectively removed from seawater using reverse osmosis. However, these results do not directly apply to hydraulic fracturing wastewaters which contain high concentrations of boron as well as other inorganic constituents, organic compounds, and microorganisms [11,14–16]. On the other hand, physicochemical techniques for flowback/produced water treatment have largely focused on dispersed and soluble oil, organic compounds, naturally occurring radioactive materials, “heavy” metals, and several cations and anions but much less is known about boron treatment from oil-field wastewaters [16]. Electrocoagulation of most hydraulic fracturing wastewaters can be performed at elevated current densities in an energy efficient manner due to their high electrical conductivity [17]. Hence, small and portable electrolysis systems with short residence times can be designed for rapid field deployment making electrocoagulation a potentially promising technology for treatment of flowback/produced water including boron.

To date, boron removal by electrocoagulation has been predominantly evaluated using low salinity synthetic wastewaters to empirically determine the role of operating parameters [17–19] although limited data with actual wastewater are becoming available [7,20,21]. However, the nature of specific interactions leading to a mechanistic understanding of boron uptake during electrochemical treatment of wastewater remains elusive even though bulk measurements suggest that chemisorption of boron to aluminum precipitates is endothermic [20].

The principal objectives of this manuscript are to provide direct evidence of boron adsorption onto electrochemically generated aluminum hydroxide flocs and obtain clues to associated uptake mechanisms. Electro-coagulation experiments were performed using an actual hydraulic fracturing wastewater sample from the Eagle Ford reservoir in Southeast Texas. Floc surfaces were rigorously characterized using Attenuated Total Reflection-Fourier transform infrared (ATR-FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) to establish boron coordination.

Experiments were designed primarily to investigate boron uptake mechanisms by  $\text{Al}(\text{OH})_3$  flocs, not simply to parametrically evaluate the role of electrochemical cell operating conditions to maximize its removal.

## 2. Experiments

### 2.1. Boron measurement

Boron was quantified by D-mannitol potentiometric titrations (ASTM D-3082-79) [7,22].  $\text{KMnO}_4$  and EDTA were added prior to mannitol addition to break any organo-boron bonds, oxidize boron to borate, and chelate potentially interfering metals ions especially since aluminum was added as the electrocoagulant. Several QA/QC protocols were performed to ensure the integrity of our measurements. First, a 100 mg/L boron spike in 25,000 mg/L NaCl solution was measured by atomic absorption spectroscopy to be  $99.6 \pm 2.2$  mg/L and by D-mannitol titration to be  $98.9 \pm 0.1$  mg/L. Next, a 25,000 mg/L NaCl solution spiked with 100 mg/L boron was electro-coagulated at 5 different aluminum dosages. For each dose, boron was measured in the feed water, supernatant, and the flocs after dissolving them at low pH using HCl. Boron recovery in these 5 experiments was  $96.3 \pm 5.6\%$ . Finally, using the same floc-dissolution procedure, boron was recovered to 96.1% and 100.7% in two separate tests where it was spiked to the actual hydraulic fracturing water sample. These QA/QC tests demonstrate accurate and precise boron measurements allowing comparison of data generated over the entire duration of experimentation.

### 2.2. Sample water

A flowback/produced water sample was obtained from the Eagle Ford formation in Southeast Texas during hydraulic fracturing after water-flooding. This black calcareous shale was chosen because a 50 mile wide and 250 feet thick play at depths between 4000 and 14,000 feet is one of the most heavily drilled enhanced oil/gas recovery targets in the United States [23,24]. Several physicochemical water quality parameters were measured using reaction cell inductively coupled plasma-mass spectrometry [25] and colorimetry to establish its composition and assist with data interpretation. Selected experiments were also performed with a 25,000 mg/L NaCl solution containing 100 mg/L boron to better understand electrocoagulation mechanisms by reducing interferences from other hydraulic fracturing water components.

### 2.3. Electrocoagulation

Bench scale experiments were conducted in a 500 mL custom-made Perspex cell fitted with an annular electrode geometry comprised of a 15 cm (9 cm submerged, initial effective area of  $20.26 \text{ cm}^2$ ) aluminum anode (99.95% metal basis, Alfa Aesar) and a porous cylindrical 316-stainless steel cathode. Before each experiment, the anode was mechanically cleaned by using fine sand paper, submerged in dilute  $\text{HNO}_3$  solution for 1 h, and thoroughly rinsed with deionized water. Occasionally, the whole unit was cleaned with dilute  $\text{HNO}_3$ . Electrocoagulation performance is known to be a strong function of reactor design including geometry, number, spacing, and type of electrodes, current density, background water composition, and numerous other operational parameters [26–28]. Since a variety of bench-scale cell configurations have already been used to empirically determine boron removal, tests were designed to better understand removal mechanisms, not simply to maximize removal. Initial experiments were conducted at pH 6.4 and 8.0, high current densities (20, 50, and  $80 \text{ mA/cm}^2$ ), and aluminum dosages <1400 mg/L to evaluate boron

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